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SUMMARY

1. PURPOSE. To provide security and policy review on the document at Tab 1 prior to release to the public.

2. BACKGROUND.

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Title: Symmetrical Bis(fulvene) Chromophores: Model Compounds for Acceptor-Donor-Acceptor Dye Architectures

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Thesis/Dissertation Book Other: _____

Description: A facile method for synthesizing conjugated bisfulvenes demonstrate tailorable optical band gaps and serve as model dye systems for new organic electronic applications.

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3. DISCUSSION. N/A

4. VIEWS OF OTHERS. N/A

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1 Tab
Manuscript with Graphical Abstract

Symmetrical Bis(fulvene) Chromophores: Model Compounds for Acceptor-Donor-Acceptor Dye Architectures†

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Four model bis(pentafulvene) chromophores have been prepared with a (fulvene)A- π -D- π -(fulvene)A architecture. Conjugation of the central donor group with the pendant fulvene rings was apparent from a single crystal X-ray study of the bis(pentafulvene) with 2,5-dihexyloxyphenyl as the central donor group. UV-Vis results indicated a tunable bandgap in the range of 400–700 nm by varying the nature of the central donor in this series of dyes.

The synthesis of donor- π -acceptor (D- π -A) organic molecules continues to have a significant impact on developments in the expanding molecular electronics industry. Recent review articles highlight some of this work including applications directed at luminescent devices such as organic light emitting diodes (OLEDs) and sensors,¹ field-effect transistors (FETs),² and dye sensitized solar cells (DSSCs).³ Linear D- π -A type structures, containing an electron rich donor group connected through a π bridge to one acceptor group, have been the mainstay of design for these molecules. Other architectures, in which the geometric disposition of donor and/or acceptor groups is variable around a central core, have also emerged and proven as flexible designs. Examples include V-shaped D- π -A- π -D,⁴ star shaped (D- π)₃A,⁴ star shaped (A- π)₃D,^{5,6} and linear A- π -D- π -A molecules.^{7,8} Versatility in the tuning of electronic absorption and charge transport properties is a clear advantage to the use of these designs.

Substituted pentafulvene frameworks offer unique possibilities as D- π -A molecules with tunable properties. As an example, the placement of various electron withdrawing substituents on the cyclopentadiene ring of 6-(*p*-dimethylamino) and 6-(1,3-dithiole-2-ylidene) donor-substituted pentafulvenes showed a significant influence on photophysical and electrochemical properties.⁹ In addition, cyano substituted pentafulvenes have been the focus of particular attention due to their useful properties for possible application as electron transport materials in bulk heterojunction solar cells.^{10–13} Stimulated by these results and as an extension of our systematic study of 1,3-diphenyl-6-substituted fulvene chromophores,¹⁴ we are exploring the possibility of using multiple pentafulvenes as pendant acceptor groups conjugated to a central electron donating group. In this work, we report the synthesis,

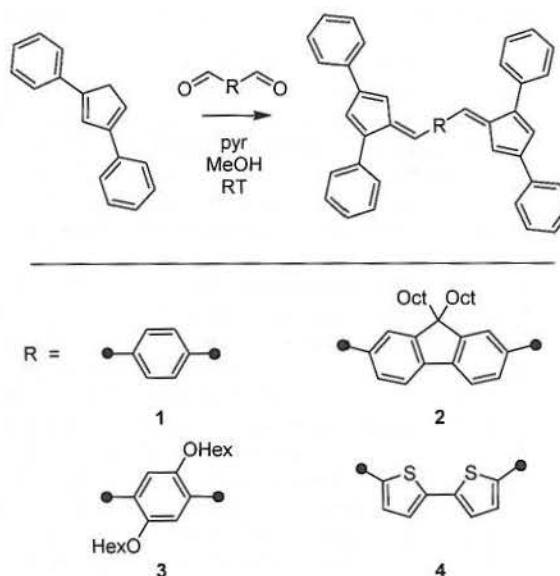


Fig. 1. Preparation of bis(fulvene) compounds.

spectroscopic properties and computational results of four new model dyes (Figure 1) of the (fulvene)A- π -D- π -(fulvene)A design, and demonstrate tunable optical properties in this series by varying the central electron donating group. A structural study of one of these dimer molecules shows enhanced conjugation of the pendant fulvenes with the electron donating group compared to a structurally related monomer compound. The model compounds presented here represent a new approach for incorporation of the pentafulvene framework into D- π -A systems,¹⁵ and provides greater opportunity for tuning the electronic and other properties important for application in functional organic electronics.

The synthesis and spectroscopic analysis of dyes 1–4 (Figure 1) follows from our recent work on 6-substituted 1,3-diphenylfulvenes¹⁴ only using 1,4-dialdehydes of aromatic and heteroaromatic groups such as benzene, 2,5-dihexyloxybenzene, 9,9'-dioctylfluorene and 2,2'-bithiophene. The bis(fulvenes) 1–4 were isolated as deeply colored air and light stable crude solids by vacuum filtration from the reaction mixtures under ambient

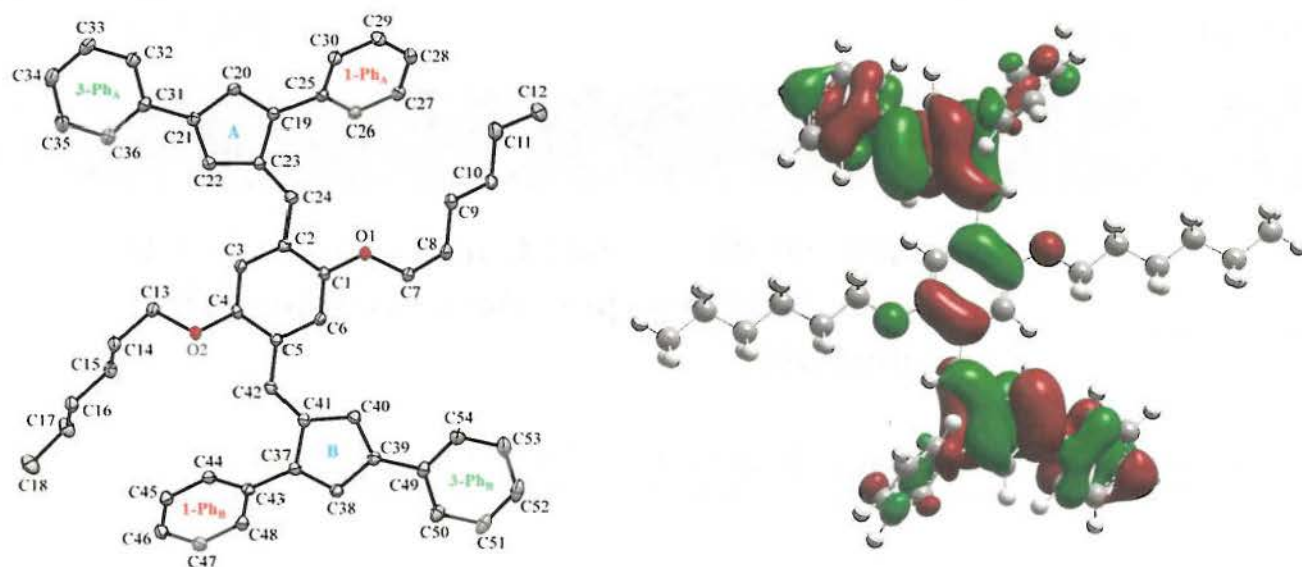


Fig. 2 Molecular structure of bis(fulvene) **3** (left) compared to the calculated (DFT, HOMO) structure (right). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms on the thermal ellipsoid view were omitted for clarity.

conditions, followed by washing with MeOH and vacuum drying. Compound **4** was obtained pure (^1H NMR) by this method, but the other compounds required purification by chromatography (**1–3**). Spectroscopic characterization of bis(fulvenes) **1–4** was carried out using ^1H and ^{13}C NMR as well as HRMS analysis. Proton NMR peaks (CDCl_3) for the four Cp H's of **1** and **2** occurred as two multiplets in the range of δ 6.9 – 7.1 similar to the pattern for 1,3,6-triphenylfulvene reported previously.¹⁴ Single peaks in the ^1H NMR spectra of **3** and **4**, that do not overlap with peaks from the PhH's and central donor group H's, were observed at δ 6.95 (**2**) and δ 6.93 (**4**), but could not be unambiguously assigned to the Cp H's or the fulvene exocyclic-CH's. The ^{13}C NMR spectra of **1–4** gave the correct number of peaks at the expected chemical shifts consistent with the symmetrical bis(fulvene) structures. Details of all syntheses and spectroscopic data are found in the supporting information.

A single crystal X-ray diffraction study¹⁶ was carried out on compound **3**, and the molecular structure is shown in Figure 2. Tables of all derived parameters as well as packing views are given in the supporting information. Bis(fulvene) **3** adopts a non-centrosymmetric dimer structure with two unique and mutually *trans*-1,3-diphenylfulvene groups (A and B, Figure 2) attached to a bis(1,4-O-hexyl)Ph spacer. Structural parameters show a central ((sp^2)O-hexyl)Ph electron donating group with conjugation extending through both fulvene systems onto two periphery Ph rings (3-Ph_A and 3-Ph_B, Figure 2). Conjugation of both fulvene rings of the dimer **3** to the central (O-hexyl)Ph group is reflected in the angles between the mean plane of the central Ph group and the fulvene ring planes A ($14.27(10)^\circ$) and B ($20.77(9)^\circ$), which are both small compared to the corresponding angle found in the structurally related and monomeric 1,3-diphenyl-6-(2,5-dimethoxyphenyl)fulvene ($45.75(5)^\circ$).¹⁴ Although the tilt angles for the 1-Ph_A and 1-Ph_B rings with respect to the A ($40.05(7)^\circ$) and B ($44.27(5)^\circ$) fulvene rings are large and comparable to the corresponding angle for 1,3-diphenyl-6-(3,5-dimethoxyphenyl)fulvene ($45.75(4)^\circ$),¹⁴ the tilt angles for the 3-Ph_A and 3-Ph_B rings with respect to the A ($5.41(2)^\circ$) and B ($16.64(10)^\circ$) fulvene planes are smaller compared to 1,3-diphenyl-6-(3,5-dimethoxyphenyl)fulvene ($24.11(5)^\circ$).¹⁴ A notable feature of the structure is the correlation of this pattern of conjugation with the calculated electron probability distribution shown in the HOMO and

LUMO plots (Figure 2 and supporting information). To our knowledge, bis(fulvene) **3** represents the first example of a non-Diels-Alder pentafulvene dimer linked and conjugated with an electron rich central group that has been characterized by single crystal X-ray diffraction.

All solid products **1–4** are intensely colored materials ranging from dark orange (**1**) to black (**4**). UV-Vis studies of **1–4** were carried out (THF, 0.3–0.8 mM) in order to compare and correlate λ_{max} values with structure and the nature of the central electron donating group. Comparison of the absorption spectrum of the monosubstituted 1,3-diphenyl-6[5-(2,2'-bithiophene)]fulvene¹⁴ to bis(fulvene) **4** (Figure 3 and Table 1) showed a significant red shift for **4** ($\Delta\lambda_{\text{max}} = 70$ nm), and points to an advantage of the acceptor-donor-acceptor over the simple donor-acceptor structure. Similar observations were made for compounds **1** and **2** and their monofulvene counterparts which have been previously studied (Table 1). In the bis(fulvene) series, the spectra show a progressively red shifted trend in λ_{max} values from 405 nm (**1**) to 509 nm (**4**) (Figure 4, Table 1). In addition, the lowest energy onset absorption is extended to 700 nm for the electron-rich groups indicating a lower energy HOMO-LUMO bandgap for these model dyes. Although bis(fulvenes) **1–4** exhibited strong solution absorption spectra, they failed to emit upon excitation ($\lambda_{\text{exc}} = \lambda_{\text{max}}$, THF), indicating a highly flexible solution structure for these model compounds.

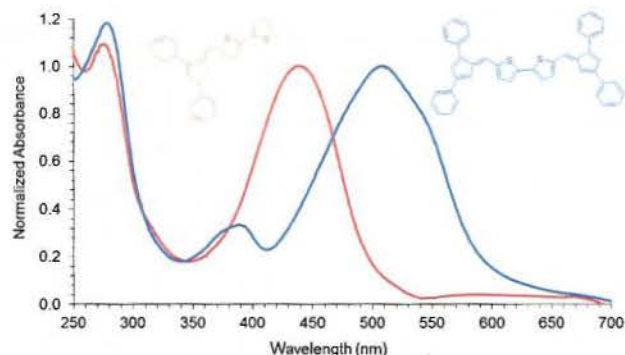


Fig. 3 Red shift of bis(fulvene) **4** (blue spectrum) compared to 1,3-diphenyl-6[5-(2,2'-bithiophene)]fulvene (red spectrum).

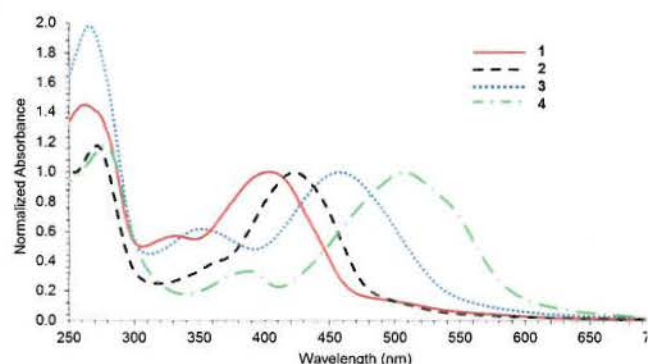


Fig. 4 Trend in λ_{\max} values for bis(fulvene) series 1–4.

Table 1. Selected fulvene solution electronic properties.

Fulvene	λ_{\max}	$\log(\epsilon)^a$	$\Delta\lambda_{\max}^b$	ΔE_{opt}^c	ΔE_{calc}^d
1	405	4.45	60	2.61	2.13
2	424	4.39	39	2.55	2.46
3	457	4.44	–	2.27	2.16
4	509	4.41	70	2.08	1.91

[a] ϵ values reported in $\text{L mol}^{-1} \text{cm}^{-1}$. [b] Difference between λ_{\max} values of bis(fulvene) (1) and 1,3,6-triphenylfulvene, (2) and 1,3-diphenyl-6-(2-fluorenyl) fulvene, and (4) and 1,3-diphenyl-6-[5-(2,2'-bithiophene)]fulvene. [c] Estimated by onset of absorption. [d] DFT results.

In order to further probe the electronic structure of bis(fulvenes) 1–4 cyclic voltammetry experiments (CV) and density functional theory (DFT) computational studies were carried out. A CV scan of bis(fulvene) 1 (CH_2Cl_2 , Bu_4NPF_6) in the range of -1 to $+1$ V gave a reduction wave, but reversibility was precluded presumably due to the reactivity of fulvene radical anions produced in the reduction. Bis(fulvene) 2 showed a similar behaviour, so additional CV experiments of 1–4 were abandoned. However, further study of this behaviour for bis(fulvenes) is pending in our group, as it has potential implication for higher order structures. In the DFT study (see supporting information), all four molecular geometries were optimized with no imaginary vibrational frequencies. The gas phase geometries show a 22 – 29° angle between the central Ph group and the fulvene ring planes, somewhat larger than observed in the crystal structure of bis(fulvene) 2 (vide supra). Calculations of the UV-vis spectra show an average deviation of 35 nm for the predicted λ_{\max} of the lowest energy peak (Table 1). However, because the HOMO-LUMO transition typically has a lower extinction coefficient, the HOMO-LUMO gap does not necessarily track with λ_{\max} (Table 1). Plots of the HOMOs and LUMOs for 1–4 are shown in the supporting information. The plots show that the fulvene moiety contains significant HOMO and LUMO electron probability for all four bis(fulvene) derivatives, although in 4, the thiophene ring also has significant electronic population. In 4, both the HOMO and LUMO extend over most of the molecule, whereas in the other molecules, both the HOMO and LUMO are more localized. This may account for the relatively low HOMO-LUMO gap of bis(fulvene) 4.

Four new bis(pentafulvene) dyes with a (fulvene)A- π -D- π -(fulvene)A design and containing a variety of electron-rich cores have been prepared and characterized using NMR, single crystal X-ray, HRMS, and UV-Vis techniques. The ability to tune the optical properties of these dyes points to an effective and versatile architecture for incorporation of the substituted pentafulvene unit into D- π -A systems. The scope of the synthetic methodology can be

easily expanded in terms of both the nature of the central donor and the nature and arrangement of substituents on the pendant fulvene rings. Furthermore, we anticipate that the presence of two or more fulvene rings as pendant groups will be an advantage in the design of novel dyes for multiple attachment sites to semiconductor surfaces or for functionalization as monomer units towards the synthesis of conjugated pentafulvene based polymers. Research directed towards these goals as well as structure property relationships of new and novel pentafulvene D- π -A molecular architectures is on-going in our lab.

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Notes and references

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- [†] Electronic Supplementary Information (ESI) available: Experimental details for the synthesis of bis(fulvenes) 1–4, figures of ^1H and ^{13}C NMR spectra, text describing crystallographic details for bis(fulvene) 4, crystallographic tables, thermal ellipsoid packing views, cif for 4, DFT computational details, calculated UV-Vis spectra and HOMO and LUMO plots for bis(fulvenes) 1–4. See DOI: 10.1039/c0000000x.
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- A Japanese patent (Matatoshi, N.; Kazuhiro, E. *Jpn. Kokai Tokkyo Koho* **2006**, JP 2006024655 A 20060126) describes the construction of an electroluminescent device using compounds consisting of an electron donor with pendant pentafulvenes.
- Crystal data for 4 (100 K): $\text{C}_{34}\text{H}_{34}\text{O}_2$, MW = 734.97; triclinic, P-1 [a = $10.0302(19)$ Å, b = $14.195(3)$ Å, c = $15.533(3)$ Å, V = $2069.2(7)$ Å³, Z = 2]; D_c = 1.180 ; 43327 reflections collected, ($2\theta_{\max}$ = 56°), 9982 unique, (R_{int} = 0.0569); Bruker SMART APEX CCD; Mo K α , λ = 0.71073 Å; final GOF = 1.022 , $R1$ = 0.0505 , $wR2$ = 0.1198 [$I > 2\sigma(I)$]; structure solved using direct methods; refinement, full matrix least squares on F^2 .

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A facile method for synthesizing conjugated bisfulvenes demonstrate tailorable optical band gaps and serve as model dye systems for new organic electronic applications

